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## **$^1\text{H}$ NMR Study of the Solvation and Gelation in a Poly(vinyl alcohol)/DMSO- $\text{d}_6$ /H $_2\text{O}$ System**

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The solvation and the gelation have been examined for poly(vinyl alcohol) (PVA)/deuterated dimethyl sulfoxide (DMSO- $\text{d}_6$ )/H $_2\text{O}$  solutions by  $^1\text{H}$  NMR spectroscopy. At water contents less than about 20 wt%, the triplet of OH protons assignable to *mm*, *mr*, and *rr* triads can be clearly observed, indicating that no H-H exchange occurs between OH groups of PVA and water molecules. In contrast, broadening and collapsing of the OH triplet are observed at the water contents higher than 24.5 wt% as a result of the H-H exchange. The gelation process can be also clearly followed as changes in intensities of the respective resonance lines of PVA. On the basis of these results, the gelation process of this system is briefly discussed.

KEY WORDS:  $^1\text{H}$  NMR/ Poly(vinyl alcohol)/ Tacticity/ Proton exchange/ Effect of water/ Solvation/ Gelation/ Gels/

### **INTRODUCTION**

Dimethyl sulfoxide (DMSO) and water are solvents for almost atactic poly(vinyl alcohol) (PVA) prepared by a conventional radical polymerization of vinyl acetate. However, it is well known that relatively concentrated PVA solutions prepared by mixing these two solvents in appropriate proportions gradually reduce their fluidity and become gels, for example, when they are allowed to stand at room temperature.<sup>1-6)</sup> This may suggest that the affinity between DMSO and water molecules would be significantly higher than the affinity between PVA and DMSO or between PVA and water.

The triad tacticity of PVA is frequently determined from the relative intensity of the OH triplet of a  $^1\text{H}$  NMR spectrum measured for its deuterated DMSO (DMSO- $\text{d}_6$ ) solution.<sup>7)</sup> In this case, although a small amount of H $_2\text{O}$  or D $_2\text{O}$  happens to be mixed into the solution under a conventional experimental condition, the OH groups of PVA may be so fully separated from H $_2\text{O}$  or D $_2\text{O}$  molecules, possibly due to the strong affinity between DMSO and water molecules, that the OH protons are not subjected to the H-H or H-D exchange with water molecules. However, such high affinity of those molecules will be affected by different factors such as the water content in DMSO, temperature, etc. and then the H-H exchange will be also recognized by  $^1\text{H}$  NMR spectroscopy.

In this paper, we have investigated the interaction among PVA, DMSO- $\text{d}_6$ , and H $_2\text{O}$  molecules by measuring  $^1\text{H}$  NMR spectra particularly as a function of

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water content. The gelation process of this system has also been followed by  $^1\text{H}$  NMR spectroscopy and discussed in relation to the solvation of PVA with DMSO and  $\text{H}_2\text{O}$  molecules.

## EXPERIMENTAL

*Sample.* PVA with a degree of polymerization of 1,700, which was provided by Kuraray Co. Ltd., was fully hydrolyzed in an aqueous alkaline solution, purified by Soxhlet extraction with methanol, and then dried in vacuum at  $50^\circ\text{C}$  for two days. Almost all PVA solutions with different  $\text{H}_2\text{O}$  contents were prepared by mixing a PVA DMSO- $\text{d}_6$  solution with an aqueous PVA solution in an appropriate proportion. The total concentration of PVA was 3 wt% in this work.

*NMR measurements.*  $^1\text{H}$  NMR measurements were performed on a JEOL JNM-GX400 NMR spectrometer under a static magnetic field of 9.4 T.  $45^\circ$  single pulse sequence was used for FID accumulation;  $45^\circ$  pulse width =  $4.5\ \mu\text{s}$ , pulse repetition delay = 60 s.  $^1\text{H}$  chemical shifts were determined by using the residual proton resonance line of DMSO- $\text{d}_6$  appearing at 2.52 ppm as an internal reference. The sample temperature was regulated to  $\pm 0.5^\circ\text{C}$  and monitored by a JEOL variable temperature unit. The temperature was calibrated by using a copper-constantan thermocouple buried in a polymer block in an NMR tube.

## RESULTS AND DISCUSSION

### *Effects of $\text{H}_2\text{O}$ on the OH Resonance Line of PVA*

Figure 1 shows 400 MHz  $^1\text{H}$  NMR spectra of PVA DMSO- $\text{d}_6$  solutions with different  $\text{H}_2\text{O}$  contents, which were measured at  $50^\circ\text{C}$ . A triplet I, II, and III of OH groups of PVA is clearly observed at 4.59, 4.39, and 4.16 ppm for the PVA solution prepared from pure DMSO- $\text{d}_6$  (Fig. 1a), although a small line assignable to  $\text{H}_2\text{O}$  protons appears at 3.24 ppm. Such a clear triplet can also be detected for the solution containing  $\text{H}_2\text{O}$  of 10.8 wt%, indicating that no H-H exchange occurs between the OH groups of PVA and  $\text{H}_2\text{O}$  molecules. This may be due to the complete separation of OH groups of PVA from water molecules probably because of the preferential solvation of DMSO molecules with OH groups of PVA and  $\text{H}_2\text{O}$  molecules. However, the OH triplets begin to increase in linewidth at the water content of 24.5 wt% and then collapse into a single broad line at 37.9 wt%. Moreover, the intensity of the broad resonance of the OH groups abruptly decreases with increasing water content. These phenomena imply that the OH protons of PVA can exchange with  $\text{H}_2\text{O}$  protons to a significant extent. The exchange frequency is estimated to be about 60 Hz at the water content of 53.8 wt% using a two-site exchange model.

In Figure 2 the chemical shifts of the OH, CH, and  $\text{CH}_2$  protons of PVA are plotted against the water content. The results of  $\text{H}_2\text{O}$  are also shown by a broken line for reference. The solid circle indicates the result of the single broad line observed for the OH groups of PVA at the water content of 37.9 wt%. As is clearly seen in this figure, the chemical shifts of the OH protons increase with increasing

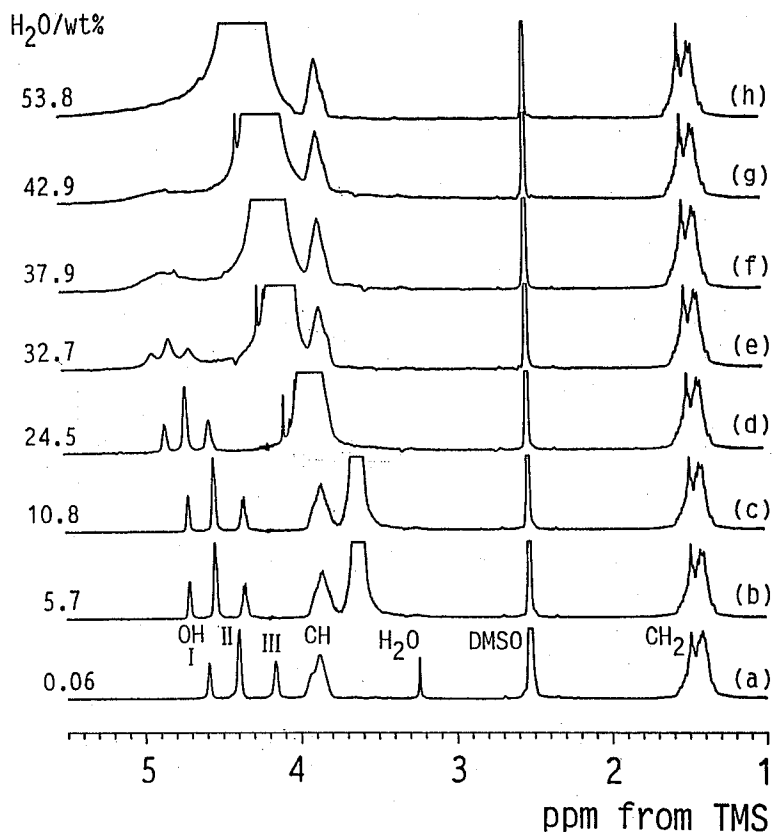


Fig. 1. 400 MHz  $^1\text{H}$  NMR spectra measured at  $50^\circ\text{C}$  for PVA DMSO- $d_6$  solutions containing different water contents.

water content, whereas those of CH and  $\text{CH}_2$  protons stay almost constant. The chemical shift of  $\text{H}_2\text{O}$  also increases with the increase of water content. Accordingly, these facts suggest that both OH groups and  $\text{H}_2\text{O}$  molecules are preferentially solvated by DMSO molecules and the deshielding of their electron clouds may be induced through the increase in the coordination number of  $\text{H}_2\text{O}$  molecules to DMSO molecules.

In Figure 3 the integrated intensities of the resonance lines I, II, and III of the OH protons are plotted as a function of water content. As is expected, each intensity stays almost constant even if the water content increases. This indicates that the existence of water less than about 20 wt% has no influence on the determination of the triad tacticities of PVA. For comparison, Table 1 shows the triad tacticities determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies. Here, the triplets of CH carbon resonances, which are assigned to *mm*, *mr*, and *rr* sequences,<sup>8)</sup> were used for estimating the triad tacticities by the complete decoupling and gated decoupling  $^{13}\text{C}$  NMR methods. The fractions determined by different methods are in good accord with each other. Moreover, since the results obtained by the two  $^{13}\text{C}$  NMR methods are almost the same, the nuclear Overhauser enhancement (NOE) induced by  $^1\text{H}$  irradiation seems not to significantly depend on the tacticities in the case of PVA

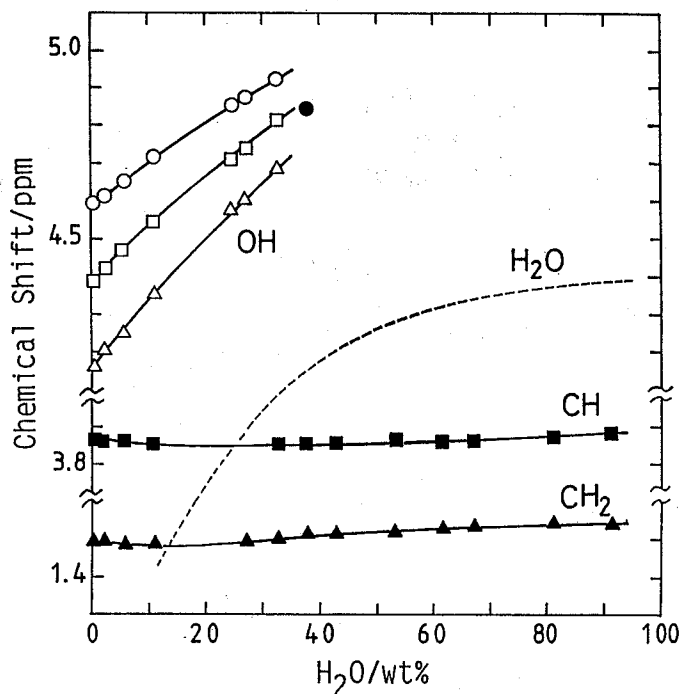


Fig. 2. Chemical shifts of OH, CH, and CH<sub>2</sub> protons of PVA as a function of the water content in DMSO-d<sub>6</sub>. The broken line indicates the dependence of the chemical shift of H<sub>2</sub>O protons on the water content.

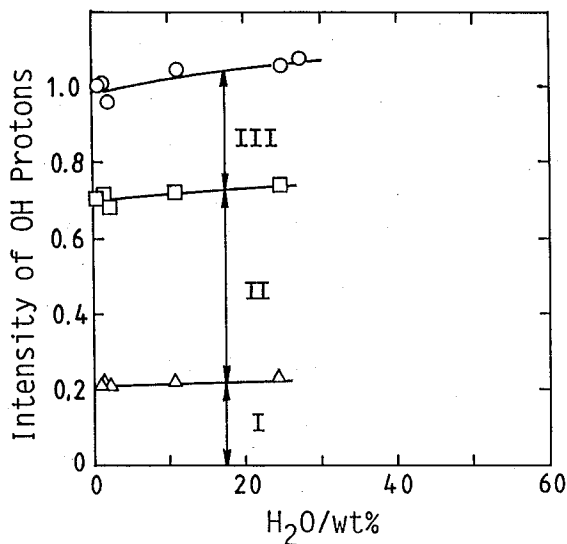
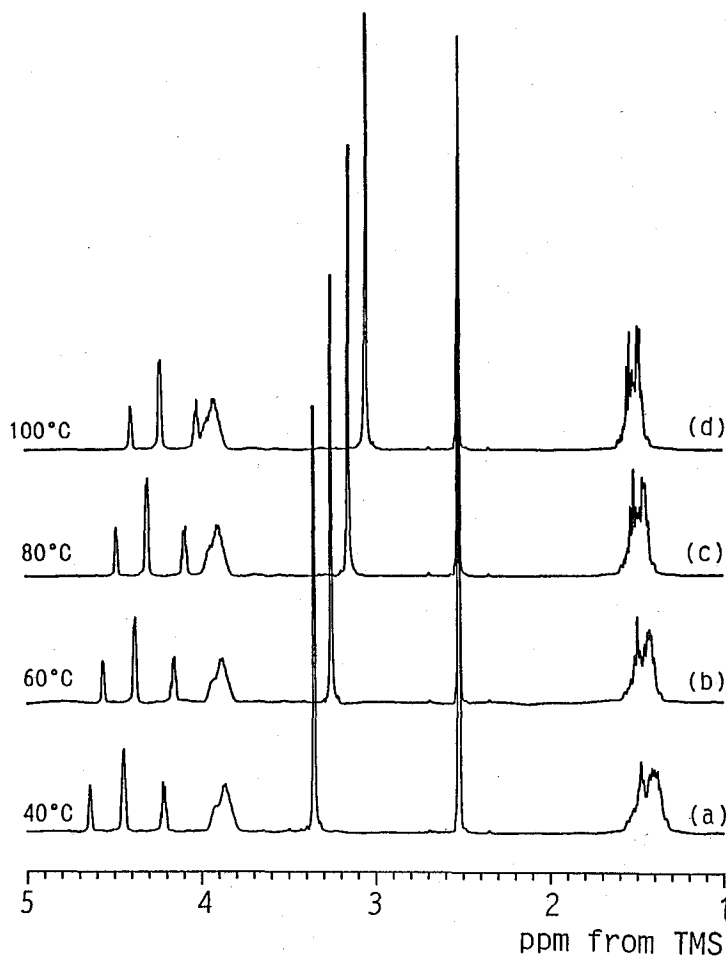


Fig. 3. Relative integral intensities of the OH triplets of PVA as a function of water content.

Table 1 Tacticities of PVA Determined in DMSO-d<sub>6</sub> Solution at 50°C by <sup>1</sup>H and <sup>13</sup>C NMR Spectroscopies.

Method	Fraction		
	<i>mm</i>	<i>mr</i>	<i>rr</i>
<sup>1</sup> H NMR	0.21	0.50	0.29
<sup>13</sup> C NMR			
complete decoupling	0.22	0.50	0.28
gated decoupling	0.23	0.50	0.27

Fig. 4. 400 MHz <sup>1</sup>H NMR spectra of the PVA DMSO-d<sub>6</sub> solution containing 1.51 wt% H<sub>2</sub>O at different temperatures.

DMSO-d<sub>6</sub> solutions.

Figure 4 shows 400 MHz <sup>1</sup>H NMR spectra of the PVA DMSO-d<sub>6</sub> solution containing 1.51 wt% H<sub>2</sub>O, measured at different temperatures. The triplets of the OH protons are clearly observed in this temperature range. This means that the

complete separation of PVA from  $\text{H}_2\text{O}$  molecules may be not changed even at  $100^\circ\text{C}$  due to their strong solvation with DMSO molecules, resulting in no observation of the H-H exchange between the OH protons and  $\text{H}_2\text{O}$  protons. In addition, almost the same spectra were also obtained at room temperature for the PVA DMSO- $\text{d}_6$  solutions heated at  $150^\circ\text{C}$  for 30 min.

It should be pointed out here that impurities involved in DMSO- $\text{d}_6$  will strongly affect the H-H exchange between the OH groups of PVA and  $\text{H}_2\text{O}$  molecules. Figure 5 shows  $^1\text{H}$  NMR spectra of PVA/DMSO- $\text{d}_6/\text{H}_2\text{O}$  solutions which were prepared by using DMSO- $\text{d}_6$  repeatedly sealed in a glass ampoule. With increasing time of such sealing, the OH triplet becomes broad and collapses into a single broad line,

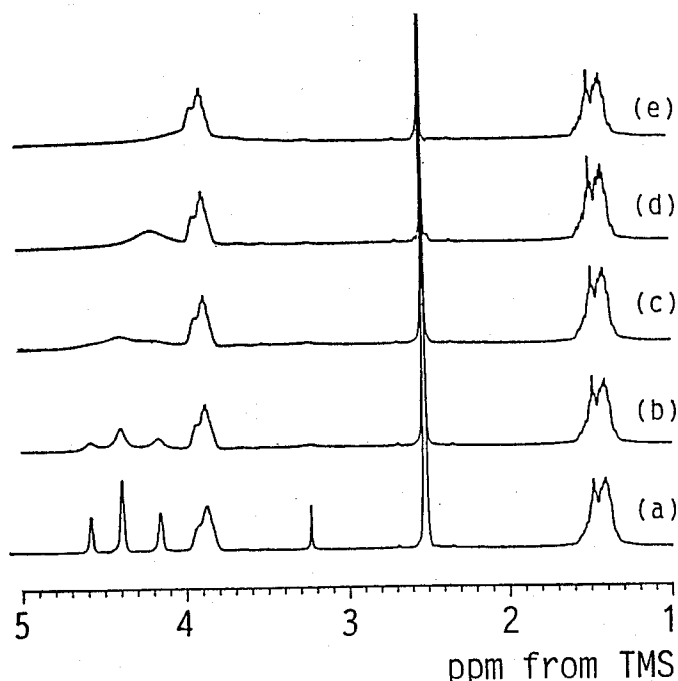


Fig. 5. Effect of the impurities involved in DMSO- $\text{d}_6$  on  $^1\text{H}$  NMR spectra of PVA DMSO- $\text{d}_6$  solutions. The repeating times for sealing of a glass ampoule: (a) 1, (b) 3, (c) 4, (d) 6, (e) 7.

which corresponds to the changes from Figure 5a to 5e. This means that some material which is probably produced by heating DMSO vapor by a gas burner and dissolved into DMSO- $\text{d}_6$  may induce the H-H exchange even at much lower water contents.

#### *Gelation Process of PVA/DMSO- $\text{d}_6/\text{H}_2\text{O}$ Solutions*

As described above, it is well known that PVA DMSO solutions containing an appropriate amount of water form gels when standing at room temperature. However, the detailed conditions and mechanism for the gelation are not well known at present. First we measured at  $30^\circ\text{C}$  the gelation rates for 3 wt% PVA solutions prepared using DMSO and  $\text{H}_2\text{O}$  as mixed solvents in different proportions. In

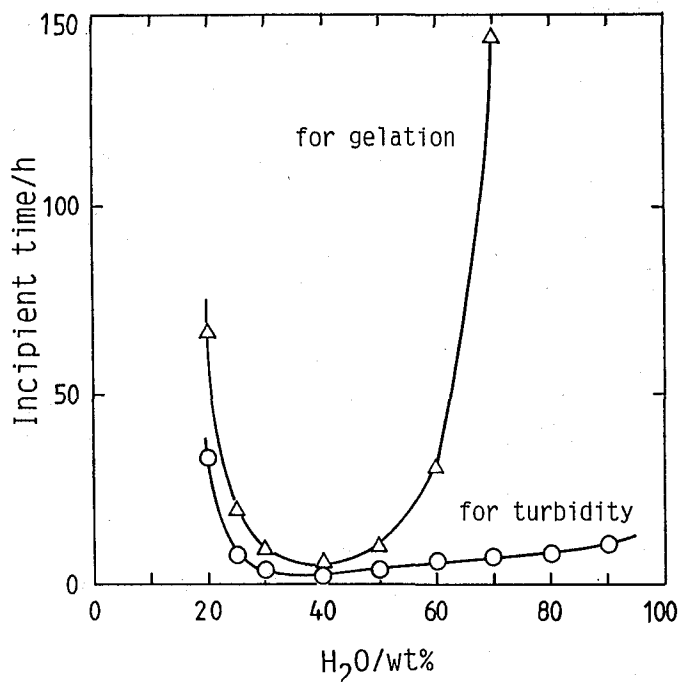


Fig. 6. Incipient times for the turbidity and the gelation of the PVA DMSO solutions with different water contents vs. water content; measured at 30°C.

Figure 6 the time required for the gelation is plotted against the water content. For comparison, the incipient time at which the solution becomes turbid is also shown in this figure. Here, the gelation time was determined as time at which the solution lost the fluidity when a glass tube containing the solution was tilted. As evidently seen in Figure 6, gels are not formed for the PVA solutions containing water less than 20 wt%. The solutions with the water contents more than 70 wt% also do not form gels although the solutions become slightly turbid within 10 h.

It should be noted here that the critical water content for the gelation, which cannot be exactly determined at present, seems to be very close to the water content where the H-H exchange begins to occur as seen in Figure 1d. This suggests that the gelation of this system may be strongly associated with the preferential interaction among the OH groups of PVA, DMSO and H<sub>2</sub>O molecules. At lower water contents all OH groups and H<sub>2</sub>O molecules are solvated by DMSO molecules, resulting in the formation of a stable solution. With increasing water content, however, part of H<sub>2</sub>O molecules may detach DMSO molecules solvating the OH groups from them to coordinate those DMSO molecules by themselves. This will lead to the formation of OH groups free from the solvation and, therefore, these OH groups may be able to aggregate with each other. Although some unknown steps might exist before the gelation, crystallites will be finally grown probably using the aggregating parts as nuclei for crystallization. The crystallites thus produced may



play a role as crosslinks in the three dimensional network for PVA gels.

When the water content increases further, some amount of water will be able to solvate the OH groups as a result of saturation of the solvation sites on the DMSO molecules. Then the gelation may be suppressed with increasing water content, depending on the extent of the limitation in the formation of the initial aggregates of PVA and the growth of the crystallites.

Figure 7 shows the changes of  $^1\text{H}$  NMR spectra in the gelation process for the PVA DMSO- $\text{d}_6$  solution containing 24.5 wt%  $\text{H}_2\text{O}$  observed at room temperature ( $\sim 27^\circ\text{C}$ ). This PVA solution becomes turbid within about 24 h, reduces fluidity, and finally becomes a gel after standing for about 45 h. Such a gelation process can be clearly observed as changes in intensities of the respective resonance lines of PVA as seen in Figure 7. In Figure 8 the relative integral intensity of  $\text{CH}_2$  protons is plotted against standing time. Here, the integral intensity was determined using the intensity of residual DMSO protons as an internal reference. The intensity decreases gradually at the initial stage but, along with the appearance of slight turbidity in the solution, the intensity abruptly decreases with increasing standing time. Although the gelation occurs after about 46 h, there appears no inflection or

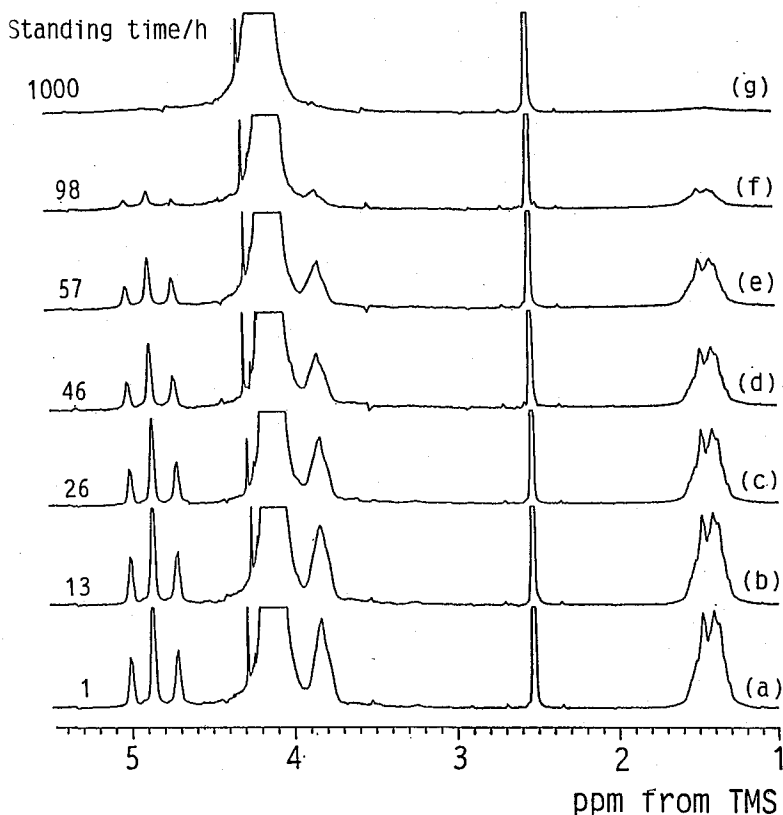


Fig. 7. 400 MHz  $^1\text{H}$  NMR spectra of the PVA DMSO- $\text{d}_6$  solution containing 24.5 wt%  $\text{H}_2\text{O}$ , measured at  $27^\circ\text{C}$  after standing for different periods.

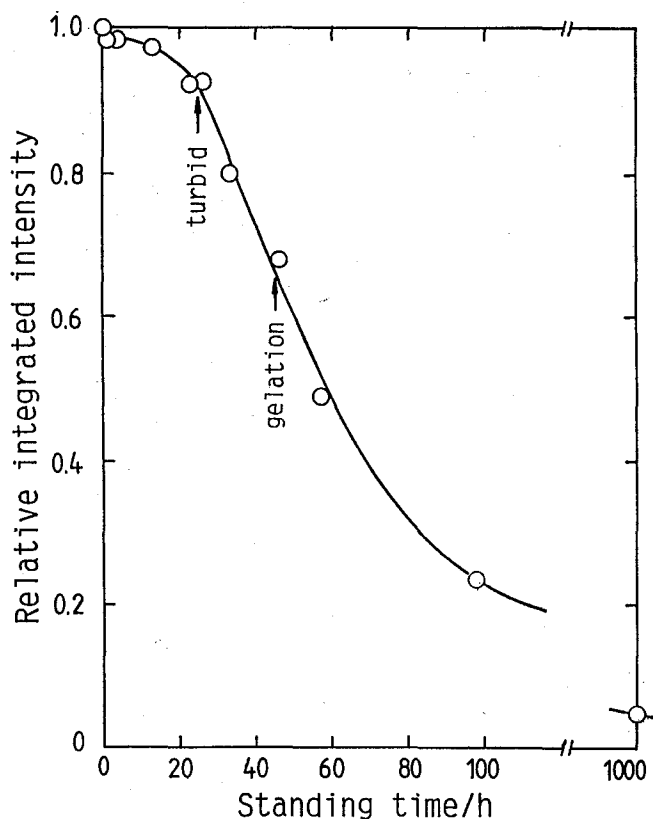


Fig. 8. Relative integral intensity of CH $_2$  protons of PVA for the DMSO- $d_6$  solution containing 24.5 wt% H $_2$ O as a function of standing time.

discontinuity on the decay curve. After standing for more than 40 days almost all resonance lines assignable to PVA protons disappear as seen in Figures 7g and 8.

In conventional  $^1\text{H}$  NMR spectroscopy high-resolution resonance lines can be observed as a result of the motional average of the dipole-dipole interaction among proton nuclei and the chemical shift anisotropy by rapid molecular motion. However, when the correlation time  $\tau_c$  of the motion attains to the order of  $10^{-4}$ – $10^{-5}$  s with decreasing molecular mobility, the resonance lines become very broad due to the dipole-dipole interaction and thus cannot be observed by the conventional NMR method. The decrease in the intensity of the CH $_2$  protons observed in Figure 8 implies therefore that some PVA segments, whose fraction corresponds to the decrease in intensity, are highly hindered in molecular mobility possibly due to the formation of the aggregates and crystallites; such immobile parts will be composed of the aggregates and crystallites and also of relatively short segments connecting aggregates and crystallites or folds associated with these structural entities. In fact, a recent wide-angle x-ray diffraction study confirmed the existence of crystallites in PVA gels prepared at room temperature from the DMSO/H $_2$ O mixed solutions with mixing ratios of 80/20–40/60.<sup>9)</sup> Diffraction peaks ascribed to (10 $\bar{1}$ ) and (101) planes of PVA

crystals were also observed for deuterated PVA gels prepared at room temperature using a DMSO- $d_6$ /D $_2$ O (60/40) mixed solvent by neutron diffraction spectroscopy.<sup>10)</sup> We have also observed a triplet with the splitting width of about 5 ppm for the CH carbon resonance line of syndiotacticity-rich PVA hydrogels by cross-polarization/magic-angle spinning (CP/MAS)  $^{13}\text{C}$  NMR spectroscopy.<sup>11)</sup> The same type of triplets appear in CP/MAS  $^{13}\text{C}$  NMR spectra of solid PVA samples with different tacticities when strong intramolecular hydrogen bonds are formed for *mm* and *mr* sequences in the crystalline and glassy noncrystalline regions.<sup>12-15)</sup> Since there may be no segment in the glassy state in the gels that are swollen with water, the triplet resonance line observed for the PVA gels indicates the existence of the same type of crystallites that are characterized for the PVA films.<sup>12-15)</sup> More detailed characterization of the gelation process and the gel structure is in progress mainly using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies.

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